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X-Ray Scattering by Atoms Using the Thomas-Fermi Model With Quantum Corrections

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Using an accurate numerical solution of the Thomas-Fermi model with quantum-mechanical corrections, we obtain a description of coherent and incoherent scattering of x-rays by the inert gases, which is in excellent agreement with detailed Hartree-Fock calculations. The results are similar to those given by the Thomas-Fermi-Dirac model, but are a substantial improvement over those given by the Thomas-Fermi model alone.

I. INTRODUCTION

Recently, a new integration technique[1] was used to obtain an accurate solution to the differential equation which determines the first-order quantum-mechanical corrections of exchange, inhomogeneity, and correlation[2,3] to the semiclassical Thomas-Fermi model of the atom,[4] and this gives a new potential field to describe the electron density about an atom. This improvement has been shown to lead to total energies of neutral atoms,[3] and diamagnetic susceptibilities and atomic polarizabilities of the inert gases,[1] among other properties, which are in substantially better agreement with experiment than are the similar values calculated by the exact Thomas-Fermi model. The purpose of this paper is to show that the improved Thomas-Fermi model also gives an excellent description of the coherent (elastic) and incoherent (inelastic) scattering of x-rays by the inert gases.

According to the Thomas-Fermi model of the atom, including the quantum-mechanical corrections, the Coulomb potential about a spherically symmetric neutral atom of atomic number Z, namely, $V(r) = -Ze^2/r$, is replaced by the modified potential

$$V(r) = \frac{-Ze^2}{bx}\left(\psi(x) + ay(x)\right) \quad , \qquad (1)$$

where $r = bx$, $a = (1/8)(6\pi Z)^{-2/3}$, $b = (6\pi)^{2/3}a_B/8Z^{1/3} = 0.88534\, a_B Z^{-1/3}$, and $a_B = h^2/me^2$ is the Bohr radius for hydrogen. $\psi(x)$ is the well known solution of the Thomas-Fermi equation[4] and is given approximately by[5]

$$\psi = \left(\frac{1 + 1.81061x^{1/2} + .60112x}{1 + 1.81061x^{1/2} + 1.39515x + .77112x^{3/2} + .21465x^2 + .04793x^{5/2}} \right)^2 , \qquad (2)$$

with a maximum error of $\delta\psi < 1.2 \times 10^{-5}$. $y(x)$ is the solution to the equation due to Kompaneets and Pavlovskii,[2,3] which gives the quantum-mechanical corrections, and using recently obtained results[1] and the fitting method of Mason,[5] we can approximate the solution with

$$y(x) = \frac{4x^{1/2} + c_1x + c_2x^{3/2} + c_3x^2 + c_4x^{5/2}}{1 + c_5x^{1/2} + c_6x + c_7x^{3/2} + c_8x^2 + c_9x^{5/2} + c_{10}x^3 + c_{11}x^{7/2}} , \qquad (3)$$

where $c_1 = -191782.81$, $c_2 = 1907451.1$, $c_3 = -5000676.6$, $c_4 = 1854931.5$, $c_5 = -45313.459$, $c_6 = 185272.21$, $c_7 = -52460.896$, $c_8 = 94265.309$, $c_9 = -31568.953$, $c_{10} = 5240.8820$, and $c_{11} = -5083.7600$, with a maximum error of $\delta y < .02$, or $a\delta y \lesssim 1 \times 10^{-4}$ for $z > 10$.

II. COHERENT SCATTERING

The differential cross section for coherent elastic x-ray scattering by an atom is given by[4,6]

$$d\sigma_{coh} = t(\theta)[F(\theta,E,Z)]^2 d\Omega , \qquad (4)$$

where $t(\theta)d\Omega$ is the differential cross section for classical Thomson scattering, given by[6,7]

$$t(\theta)d\Omega = \frac{1}{2} r_o^2 (1 + \cos^2\theta) 2\pi \sin\theta d\theta \quad , \tag{5}$$

where $r_o = e^2/mc^2$ is the classical radius of the electron and θ is the scattering angle. The form factor is defined by[4]

$$F(k) = F(\theta,E,Z) = \int \rho(r) \frac{\sin kr}{kr} dV \tag{6}$$

where the integral is over all space, ρ is electron density given by Poisson's equation

$$\rho(r) = - \frac{1}{4\pi e^2} \nabla^2 V(r) \quad , \tag{7}$$

and k is a wave number

$$k = \frac{4\pi}{\lambda} \sin \frac{\theta}{2} = \frac{4\pi E}{12.372} \sin \frac{\theta}{2} \quad , \tag{8}$$

with λ the wavelength of the x-ray in $\mathring{A} = 10^{-8}$ cm and E the energy in keV. Combining Equations (6), (7), and (1), we obtain

$$F = Zf = Z \int_o^{x_1} \frac{d^2}{dx^2} \left(\psi(x) + ay(x)\right) \frac{\sin ux}{u} dx \quad , \tag{9}$$

where $u = kb = .47586\ EZ^{-1/3}\sin\frac{\theta}{2}$, and x_1 is the radius of the atom.[1]

We shall now integrate Equation (9), but we first simplify it by integrating by parts and by using the appropriate boundary conditions[1] to obtain

$$f(u) = F/Z = 1 + \left(\psi(x_1) + ay(x_1)\right)\left[\frac{\sin ux_1}{ux_1} - \cos ux_1\right]$$

$$- u\int_0^{x_1}\left(\psi(x) + ay(x)\right)\ \sin ux\ dx \qquad . \qquad (10)$$

Using care in integration due to the oscillatory nature of the integrand in Equation (10), we obtain an evaluation of the atomic form factor divided by atomic number as a function of the scattering parameter u. The results are given in Table I for the inert gases. Also included are results for the Thomas-Fermi atom, which are Z-independent and are obtained by setting $a = 0$ and $x_1 = \infty$ in Equation (10). These latter values are in good agreement with the approximate Thomas-Fermi solution given originally by Bewilogua,[8,9] but are significantly different from our values, especially for low Z. The form factor has been calculated previously by Thomas and Umeda[10] using the Thomas-Fermi-Dirac model and these results are in close agreement with ours.

Using the atomic form factor, we can calculate the total cross sections for the coherent elastic scattering of x-rays by the inert gases. This is done by integrating Equation (4) over all angles

$$\sigma_{coh} = \int t(\theta)\ [F(\theta,E,Z)]^2\ d\Omega$$

$$= \pi r_o^2 Z^2 \int_{-1}^{1} (1 + \mu^2) f^2(u) d\mu \quad , \tag{11}$$

where f(u) is given by Equation (10) and $u = .33648\ EZ^{-1/3}\sqrt{1-\mu}$ and $\mu = \cos\theta$. The results are presented in Table II for Ne^{10}, Ar^{18}, Kr^{36}, and Xe^{54} as a function for x-ray energy over the range of 1 keV to 1000 keV. Included for comparison are the best available theoretical results, as obtained by Storm and Israel[9,11] using Hartree-Fock-Slater wave functions.[12-14] Note the agreement between the two sets of results over all energies for Ne is good at least to 20% for Ne, to 10% for Ar, to 4% for Kr, and to 2% for Xe. The rapidly decreasing error with increasing atomic number indicates that the electron density distribution is being better approximated by the given statistical model when more electrons are present.

III. INCOHERENT SCATTERING

The differential cross section for incoherent x-ray scattering from a free atom with Z electrons is given by[8,15,16]

$$\left(\frac{d\sigma}{d\Omega}\right)_{inc} = ZS(k)\left(\frac{d\sigma}{d\Omega}\right)_{fr} \tag{12}$$

where

$$S(k) = \frac{1}{Z}\left(\sum_{n,m} \left\langle \psi_o \middle| e^{i\vec{k}\cdot(\vec{r}_n - \vec{r}_m)} \middle| \psi_o \right\rangle - |F(k)|^2\right) \tag{13}$$

is the incoherent-scattering factor, where

$$F(k) = \sum_n \left\langle \psi_o \left| e^{i\vec{k}\cdot\vec{r}_n} \right| \psi_o \right\rangle \qquad (14)$$

is the coherent-scattering factor, given earlier as Equation (6), and ψ_o is the ground state wave function of the atom. The term $(d\sigma/d\Omega)_{fr}$ is the scattering cross section for a free electron at rest. At low incident photon energies, this is the Thomson cross section given by Equation (5), and at high incident photon energies, this is the Klein-Nishina scattering cross section.[6]

It has been shown that Equation (13) can be written as[15,16]

$$S = 1 - \frac{1}{Z}\left(\frac{8\pi}{3h^3}\right)\int dV \left(P_F(r) - \frac{kh}{4\pi}\right)^2 \left(P_F(r) + \frac{kh}{8\pi}\right) \quad , \qquad (15)$$

where dV is the spatial volume element, and

$$P_F(r) = \frac{h}{2}\left(\frac{3}{\pi}\right)^{1/3} \rho^{1/3}(r) \qquad (16)$$

is the local Fermi momentum. Using Equations (7) and (1) for the electron charge density, we can rewrite Equation (15) as

$$S = 1 - \int_{x_a}^{x_b} x^2 dx \left\{\left[\frac{1}{x}\frac{d^2}{dx^2}\left(\psi(x)+a y(x)\right)\right]^{1/3} - w\right\}^2 \left\{\left[\frac{1}{x}\frac{d^2}{dx^2}\left(\psi(x)+a y(x)\right)\right]^{1/3} + \frac{w}{2}\right\} \quad ,$$

(17)

where $w = bk/(6\pi Z)^{1/3}$ and x_b is determined by the condition

$$\frac{1}{x_b}\frac{d^2}{dx^2}\left(\psi(x_b) + ay(x_b)\right) = w^3 \quad . \tag{18}$$

At very small values of w, which corresponds to large x_b, we must set $x_b = x_1$, where x_1 is the radius of the atom as determined earlier.[1] For mathematical rigor, we have accounted for the divergent (and negative) behavior of

$$\frac{d^2}{dx^2}(\psi + ay) \to (1 + \frac{3}{2} aa_2)x^{-1/2} - ax^{-3/2} \tag{19}$$

at very small values of x. Requiring the electron density to be positive means that in Equation (17)

$$x \geq x_a \equiv \frac{a}{1+3aa_2/2} \quad . \tag{20}$$

However, x_a is a very small value ($x_a = .0039$ for Ne and $x_a = .0012$ for Xe) and extending the lower limit of integration to 0 in Equation (17) only has an effect of the order of $\Delta S \sim a x_a^{1/2} \lesssim 1 \times 10^{-4}$, since the integral is convergent.

Using Equation (17), we have presented in Table III values of ZS(k) for the inert gases as a function of wave number k (in Å), along with corresponding values obtained from Hartree-Fock calculations.[17] Note that for $k > 1.0$ Å, all of our values are within 2% of the Hartree-Fock values, and that for $k > 0.5$ Å, all the values are with 10%. Comparing

with the results of Mendelsohn and Biggs,[16] we further note that our values are all within 2% of the corresponding Thomas-Fermi-Dirac values. But, for the high-Z inert gases, Kr and Xe, and for $k > 1.0$ Å, our values are closer than the Thomas-Fermi-Dirac values to the Hartree-Fock results by at least a factor of two. Thus, except for the high-Z, high energy region, the present quantum-mechanical model and Thomas-Fermi-Dirac model are very similar, mainly because they both account for exchange, which is the major quantum-mechanical effect neglected in the Thomas-Fermi model. Furthermore, the present model is a substantial improvement over the Thomas-Fermi model alone, especially at low energies, as shown by Cromer and Mann,[17] Pohler and Hanson,[18] and Parks and Rotenberg.[19]

In conclusion, we find our first-order quantum-mechanical model of the atom to be quite similar to the Thomas-Fermi-Dirac model, and in very good agreement with the best available Hartree-Fock model for the calculation of coherent and incoherent x-ray scattering by the inert gases.

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Table I

Atomic Form Factors Divided by Atomic Number for the Inert Gases Using the Quantum-Mechanical Model and the Thomas-Fermi Model

u	f_{QM}				f_{TF}
	Ne	Ar	Kr	Xe	
0	1.000	1.000	1.000	1.000	1.000
.1	.982	.978	.973	.970	.953
.2	.933	.919	.904	.897	.876
.3	.863	.842	.824	.818	.799
.4	.787	.765	.750	.746	.728
.5	.715	.697	.687	.682	.666
.6	.652	.639	.629	.624	.611
.8	.553	.543	.533	.530	.519
1.0	.475	.465	.459	.456	.452
1.2	.412	.405	.399	.397	.390
1.5	.341	.335	.331	.329	.324
2.0	.258	.254	.252	.251	.247
2.5	.203	.201	.200	.199	.197
3.0	.165	.164	.163	.162	.161
3.5	.137	.137	.136	.136	.135
4.0	.117	.116	.116	.116	.116

Table II

Total Coherent Scattering Cross Sections (in barns)

for the Inert Gases Using the Quantum-Mechanical

Model and the Hartree-Fock-Slater Model

	Ne		Ar		Kr		Xe	
E(keV)	QM	HFS[9]	QM	HFS[9]	QM	HFS[9]	QM	HFS[9]
1	61.1	63.4	200.	201.	813.	818.	1840.	1840.
2	49.9	56.6	169.	172.	712.	730.	1640.	1640.
3	39.8	48.1	140.	141.	610.	633.	1440.	1420.
4	32.2	39.8	116.	116.	524.	548.	1260.	1240.
5	26.6	32.7	98.2	96.3	453.	478.	1100.	1090.
6	22.2	27.0	83.7	82.1	395.	421.	972.	961.
8	16.2	19.0	63.0	63.0	308.	333.	773.	762.
10	12.4	14.0	49.1	50.4	246.	266.	628.	618.
15	7.18	7.84	29.5	31.1	154.	163.	404.	404.
20	4.69	5.11	19.7	20.6	106.	110.	283.	288.
30	2.46	2.71	10.6	11.0	59.1	62.2	161.	163.
40	1.51	1.67	6.65	6.96	37.9	39.7	104.	106.
50	1.03	1.12	4.56	4.81	26.3	27.5	73.2	74.9
60	.739	.809	3.32	3.52	19.4	20.1	54.2	55.7
80	.435	.475	1.98	2.09	11.7	12.1	33.2	33.7
100	.285	.312	1.31	1.38	7.84	8.00	22.4	22.3
200	.0745	.0819	.347	.369	2.12	2.15	6.14	6.08
400	.0189	.0214	.0886	.0960	.547	.555	1.60	1.57
600	.00843	.0101	.0396	.0427	.245	.250	.716	.706
1000	.00304	.00379	.0143	.0156	.0885	.0910	.259	.257

Table III

Incoherent Scattering Factors, ZS(k), for the Inert Gases
Using the Quantum-Mechanical Model and the Hartree-Fock Model

$k(\text{Å}^{-1})$	Ne		Ar		Kr		Xe	
	QM	HF[16]	QM	HF[16]	QM	HF[16]	QM	HF[16]
.005	.136	.002	.192	.006	.281	.009	.351	.013
.01	.275	.009	.383	.024	.554	.035	.684	.052
.05	1.365	.218	1.886	.571	2.706	.812	3.312	1.194
.10	2.580	.812	3.597	1.956	5.206	2.703	6.398	3.841
.15	3.544	1.637	5.017	3.588	7.369	4.805	9.121	6.677
.20	4.315	2.547	6.202	5.033	9.244	6.760	11.526	9.340
.30	5.488	4.269	8.094	7.377	12.383	10.157	15.642	13.892
.40	6.335	5.644	9.547	8.998	14.931	12.828	19.075	17.307
.50	6.974	6.640	10.701	10.106	17.058	14.969	22.008	20.175
.60	7.468	7.320	11.639	10.967	18.864	16.849	24.552	22.833
.70	7.860	7.774	12.415	11.726	20.420	18.562	26.786	25.324
.80	8.175	8.085	13.064	12.424	21.774	20.123	28.766	27.619
.90	8.431	8.312	13.615	13.061	22.962	21.535	30.535	29.680
1.0	8.643	8.490	14.085	13.629	24.013	22.804	32.123	31.488
1.5	9.289	9.113	15.652	15.489	27.823	27.313	38.125	37.628
2.0	9.590	9.517	16.492	16.324	30.189	29.870	42.051	41.477
3.0	9.836	9.875	17.288	17.132	32.733	32.659	46.720	46.254
4.0	9.922	9.967	17.619	17.573	34.012	33.919	49.258	49.030
5.0	9.959	9.991	17.778	17.800	34.715	34.562	50.760	50.673
8.0	9.991	10.000	17.939	17.978	35.558	35.504	52.743	52.591

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